*Journal of Organometallic Chemistry*, 352 (1988) 257–261
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# Synthesis and reactivity of 2-amino-5-nitrophenylpalladium(II) compounds

**Jose Vicente *, Jose A. Abad and Jose A. Sanchez**

*Departamento de Quimica Inorganica, Universidad de Murcia, 30071 Murcia (Spain)*

(Received March 1st, 1988)

## Abstract

Reaction of $[Pd(PPh_3)_4]$ with RBr (R = $C_6H_3NH_2$-2, $NO_2$-5) yields *trans*-$[PdBr(R)(PPh_3)_2]$. This reacts with $AgNO_3$ to give the nitrato-complex *trans*-$[Pd(ONO_2)(R)(PPh_3)_2]$, which in turn reacts with halide anions to give *trans*-$[PdX(R)(PPh_3)_2]$ (X = Cl, I) and with neutral bidentate ligands to give *cis*-$[Pd(R)(PPh_3)(L\text{–}L)]NO_3$ (L–L = 2,2′-bipyridine, 1,10-phenanthroline, 1,2-bis(diphenylphosphino)ethane). The complex *trans*-$[PdBr(R)(PPh_3)_2]$ reacts with $AgClO_4$ to give species that react with pyridine to give *trans*-$[Pd(R)(PPh_3)_2(py)]ClO_4$.

---

## Introduction

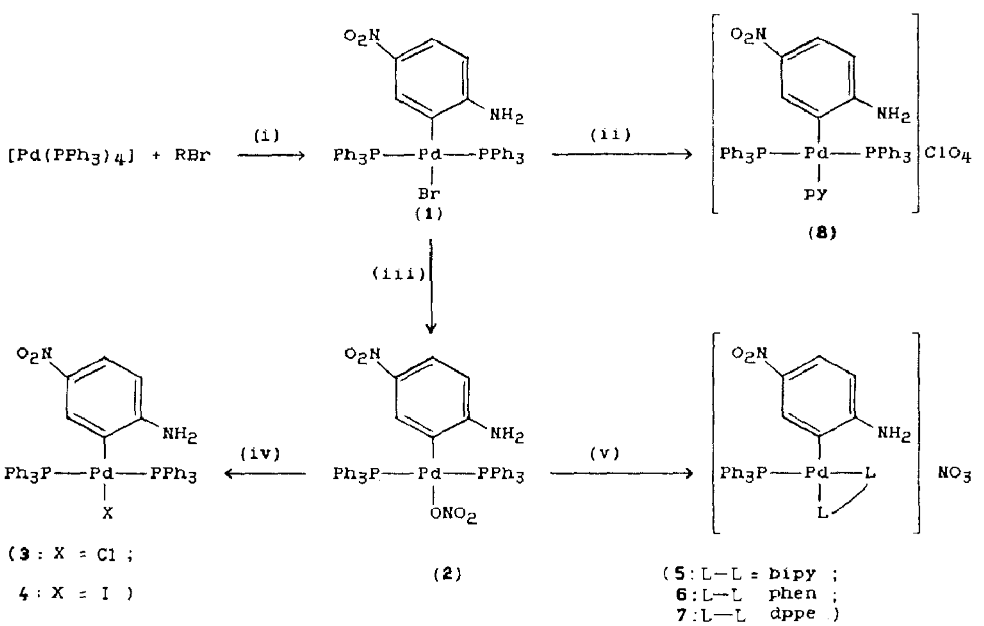
We are engaged in a study of the synthesis and reactivity of functionalized arylmetal complexes. Since they are not usually accessible through Grignard or organolithium reagents we are using organomercury compounds as transmetallation agents for the synthesis of such organo-rhodium [1], -palladium [2], -platinum [3], -gold [4], and -tin [5] complexes. In particular, we have used bis(2-amino-5-nitrophenyl)mercury to prepare the corresponding derivatives of platinum (II) [3b]; we attempted to extend the use of this reagent to the preparation of the related organopalladium complexes but were unsuccessful. Our interest in the complexes sought concerned the reactivity and coordination properties of the amino group in these complexes.

We report here the synthesis of such arylpalladium complexes through the classical oxidative addition of the relevant aryl bromide to $[Pd(PPh_3)_4]$. Although palladium complexes containing aryl groups bearing, $NO_2$, PhCO, CN, or $CO_2Me$ substituents have been reported [6], the complexes we describe here are to our knowledge the first *ortho*-aminoarylpalladium derivatives.

## Results and discussion

Refluxing a toluene solution of $[Pd(PPh_3)_4]$ with RBr (R = 2-amino-5-nitrophenyl) gave the complex *trans*-$[PdBr(R)(PPh_3)_2]$ (**1**) (see Scheme 1).

0022-328X/88/$03.50



Scheme 1. Synthesis of complexes **1–8**. (i) $-2PPh_3$; (ii) $+AgClO_4$, +py, $-AgBr$; (iii) $+AgNO_3$, $-AgBr$; (iv) $+QX$, $-QNO_3$; (v) +L–L, $-PPh_3$.

Complex **1** is not soluble enough in organic solvents for NMR studies, but its geometry can be inferred from its solid IR spectrum, which shows no band in the region 550 ± 5 $cm^{-1}$, indicating a *trans* geometry [7]. Probably owing to its low solubility, the complex is very unreactive, but it can be converted into soluble species easier to study and more reactive.

Thus, treatment of **1** with $AgNO_3$ gives the nitrato complex *trans*-$[Pd(ONO_2)(R)(PPh_3)_2]$ (**2**) (see Scheme 1). The proposed geometry for **2** is based on its $^{31}P$ NMR spectrum, which shows a singlet at $\delta$ 20.3 ppm. The absence of a band at 550 ± 5 $cm^{-1}$ in its IR spectrum suggests that it has the same structure in the solid state. The appearance of bands at 1330 and 1445 $cm^{-1}$, assignable to $\nu(A^1)(NO)_2$ and $\nu(B^1)(NO_2)$, respectively, ($\nu(B^1)-\nu(A^1) = 115$ $cm^{-1}$) suggests that the nitrate group is acting as a monodentate ligand [8].

We have used complex **2** as the source of several new organopalladium complexes. Thus, it reacts with chloride or iodide anions with precipitation of the corresponding halo derivatives *trans*-$[PdX(R)(PPh_3)_2]$ (X = Cl (**3**), X = I (**4**)) (see Scheme 1). These complexes are very similar to the analogous bromo complex, being, like **1**, almost insoluble in most common organic solvents. Complexes **1**, **3** and **4** have almost identical IR spectra, except that **3** shows a band at 300 $cm^{-1}$ assignable to $\nu$(Pd–Cl).

Complex **2** reacts with bidentate ligands such as 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) giving the cationic complexes *cis*-$[Pd(R)(PPh_3)(L-L)]NO_3$ (L–L = bipy (**5**), phen (**6**)). The reaction with 1,2-bis(diphenylphosphino)ethane (dppe) gives a complex, **7**, whose analytical data and $^1H$ NMR spectrum are consistent with the formulation $[cis\text{-}[Pd(R)(PPh_3)(dppe)](NO_3)] \cdot 0.3CH_2Cl_2$ ($\delta$ 5.3 ppm for $CH_2Cl_2$). Furthermore the signals expected in the $^{31}P\{^1H\}$ NMR spectrum

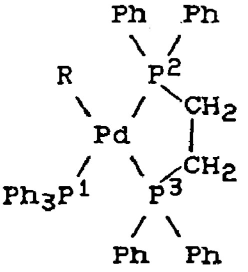


Fig. 1. Diagram showing the numbering of phosphorus atoms.

of 7 (see Fig. 1), appear at δ 22.6 ($P^1$, dd, $J(P^1P^2)$ 369 Hz, $J(P^1P^3)$ 27 Hz, 41.7 ($P^3$, dd, $J(P^2P^3)$ 21 Hz) and 48.6 ($P^2$, dd) ppm.

The nitrato-ligand in complex **2** is not replaced by neutral monodentate ligands such as pyridine (py) or triphenylphosphine. However, it is possible to prepare *trans*-$[Pd(R)(PPh_3)_2(py)]ClO_4$ (**8**) by addition of pyridine to solutions prepared from **1** and $AgClO_4$. These solutions are assumed to contain species of the stoicheiometry "$Pd(R)(PPh_3)_2(ClO_4)$" that react with pyridine to give complex **8** owing to the low coordination ability of the perchlorate ligand. The $^{31}P\{^1H\}$ NMR spectrum of **8** shows a singlet at 21.3 ppm.

Comparison of the IR spectra of *para*-nitroaniline, $HgR_2$, and complexes **1**–**8** does not give clear evidence for the assignment of the ν(NO) bands arising from the $NO_2$ group and the $NO_3$ anion, or of $\delta(NH_2)$. Two or three bands in the 3200–3500 $cm^{-1}$ region are assignable to ν(NH) (see Experimental).

Table 1 gives analytical and other data for complexes **1**–**8**. The molar conductivities of complexes **5**–**8** in acetone are consistent with their formulations as 1/1 electrolytes. The only neutral complex sufficiently soluble in acetone, namely **2**, has the expected molar conductivity.

## Experimental

Infrared spectra were recorded in te range 4000–200 $cm^{-1}$ on a Perkin–Elmer 1430 spectrophotometer by use of Nujol mulls between polyethylene sheets. Conductivities were measured for ca. $10^{-4}$ mol $dm^{-3}$ acetone solutions with a Philips 9501 conductimeter. Melting points were determined on a Reichert apparatus, and are uncorrected. C, H and N analyses were carried out with a Perkin–Elmer 240 ° C microanalyzer. NMR spectra were recorded with $CDCl_3$ solutions on a Bruker AM-400 spectrometer with TMS and external aqueous $H_3PO_4$ as references.

Reactions were carried out at room temperature with stirring and without special precautions against light or atmospheric moisture unless otherwise stated.

*trans-[PdBr(R)(PPh$_3$)$_2$] (1).* $2\text{-}NH_2\text{-}5\text{-}NO_2C_6H_3Br$ (680 mg, 3.13 mmol) was added to a suspension of $[Pd(PPh_3)_4]$ [9] (3.6 g, 3.12 mmol) in toluene (20 $cm^3$) and the mixture was refluxed for 30 min. The yellow solid was filtered off, then washed with toluene (10 $cm^3$) followed by diethyl ether to give crude **1** (2.31 g, 87% yield). An analytically pure sample was obtained by extracting the crude product with chloroform in a Soxhlet apparatus. The suspended solid was filtered off and dried at 70 ° C for 4 h. ν(NH) 3460(m), 3350(m) $cm^{-1}$.

Table 1

Analytical and other data for complexes **1–8**

| Compound | M.p. [a] (°C) | $\Lambda_M$ [b] | Analytical data (found (calc.)(%)) C | H | N |
|---|---|---|---|---|---|
| *trans*-[PdBr(R)(PPh$_3$)$_2$] (**1**) | 129 | – | 59.00 | 3.82 | 3.29 |
| | | | (59.48) | (4.16) | (3.30) |
| *trans*-[Pd(ONO$_2$)(R)(PPh$_3$)$_2$] (**2**) | 166 | 3 | 60.44 | 4.14 | 5.04 |
| | | | (60.77) | (4.25) | (5.06) |
| *trans*-[PdCl(R)(PPh$_3$)$_2$] (**3**) | 237 | – | 62.04 | 4.90 | 3.96 |
| | | | (62.78) | (4.39) | (3.49) |
| *trans*-[PdI(R)(PPh$_3$)$_2$] (**4**) | 229 | – | 56.29 | 3.86 | 3.08 |
| | | | (56.36) | (3.94) | (3.13) |
| *cis*-[Pd(R)(PPh$_3$)(bipy)]NO$_3$ (**5**) | 224 | 93 | 56.40 | 3.63 | 9.41 |
| | | | (56.40) | (3.90) | (9.67) |
| *cis*-[Pd(R)(PPh$_3$)(phen)]NO$_3$ (**6**) | 219 | 97 | 58.11 | 3.73 | 8.64 |
| | | | (57.80) | (3.77) | (9.36) |
| *cis*-[Pd(R)(PPh$_3$)(dppe)]NO$_3$ (**7**) [c] | 134 | 84 | 60.92 | 5.03 | 4.15 |
| | | | (60.92) | (4.53) | (4.24) |
| *trans*-[Pd(R)(PPh$_3$)$_2$(py)]ClO$_4$ (**8**) | 161 | 100 | 58.83 | 4.01 | 4.37 |
| | | | (59.63) | (4.26) | (4.44) |

[a] With decomposition. [b] In $\approx 10^{-4}$ *M* solutions in acetone ($\Omega^{-1}$ cm$^2$ mol$^{-1}$). [c] The calculated values are for $7 \cdot 0.3Cl_2CH_2$.

*trans-[Pd(ONO$_2$)(R)(PPh$_3$)$_2$] (2).* Solid AgNO$_3$ (20 mg, 0.12 mmol) was added to a suspension of **1** (100 mg, 0.12 mmol) in acetone (10 cm$^3$). After one day the solvent was evaporated off and the solid washed with diethyl ether, filtered off, and recrystallized from dichloromethane/n-hexane to give **2** (80 mg, 83% yield). $\nu$(NH) 3480(m), 3340(s) cm$^{-1}$.

*trans-[PdCl(R)(PPh$_3$)$_2$] (3).* Solid (PhCH$_2$PPh$_3$)Cl (41 mg, 0.1 mmol) was added to a solution of **2** (80 mg, 0.1 mmol) in dichloromethane. After 5 h the solvent was evaporated off and the yellow solid washed with ethanol (20 cm$^3$) then filtered off to give crude **3** (62 mg, 79% yield). An analytically pure sample was obtained by recrystallizing some of the crude product from dichloromethane/n-hexane, and drying at 80 °C for 15 h. $\nu$(NH) 3480(s), 3370(s) cm$^{-1}$.

*trans-[PdI(R)(PPh$_3$)$_2$] (4).* Solid NaI · 2H$_2$O (28 mg, 0.15 mmol) was added to a suspension of **2** (103 mg, 0.12 mmol) in acetone (20 cm$^3$). After 30 min, the yellow solid was filtered off, washed with water and then diethyl ether, and dried at 80 °C for two days, to give **4** (93 mg, 84% yield). $\nu$(NH) 3480(m), 3370(s) cm$^{-1}$.

*cis-[Pd(R)(PPh$_3$)(bipy)]NO$_3$ (5).* Solid 2,2′-bipyridine (13 mg, 0.09 mmol) was added to a solution of **2** (70 mg, 0.08 mmol) in dichloromethane (15 cm$^3$). After 6 h the solvent was evaporated off and diethyl ether added. The yellow solid was filtered off, recrystallized from dichloromethane/n-hexane, and dried at 80 °C for 4 h to give **5** (52 mg, 85% yield). $\nu$(NH) 3400(m), 3305(m), 3210(m) cm$^{-1}$.

*cis-[Pd(R)(PPh$_3$)(phen)]NO$_3$ (6).* This complex was prepared from **2** (107 mg, 0.13 mmol) and 1,10-phenanthroline · H$_2$O (26 mg, 0.13 mmol) by the procedure described for complex **5**. The recrystallized product was dried at 90 °C for 3 days. Yield, 93%. $\nu$(NH) 3460(m), 3280(m), 3200(m) cm$^{-1}$.

*cis-[Pd(R)(PPh$_3$)(dppe)]NO$_3$ · 0.3Cl$_2$CH$_2$ (7).* This complex was prepared from **2** (172 mg, 0.21 mmol) and 1,2-bis(diphenylphosphino)ethane (83 mg, 0.21 mmol) by the procedure as described for complex **5**. The recrystallized product was dried at 70 ° C for 6 h. Yield, 91%. $\nu$(NH) 3440(w, br), 3325(w, br), 3190(w, br) cm$^{-1}$.

*trans-[Pd(R)(py)(PPh$_3$)$_2$]ClO$_4$ (8).* Solid AgClO$_4$ (73 mg, 0.35 mmol) was added to a suspension of complex **1** (300 mg, 0.35 mmol) in acetone (20 cm$^3$) protected from light. After 7 h, the solid was filtered off and the filtrate evaporated to dryness. Acetone (10 cm$^3$) and an excess of pyridine was added to the residue and after 8 h the resulting solution was evaporated to dryness and the solid washed with diethyl ether, recrystallized from dichloromethane/n-hexane, and dried at 80 ° C for 4 h to give **8**. Yield, 86%. $\nu$(NH) 3460(w), 3360(m) cm$^{-1}$.

## Acknowledgements

We thank the Comision Asesora de Investigacion Cientifica y Tecnica (Spain) (PB85-0295) for financial support and Prof. P. Lahuerta for NMR facilities.

## References

1 J. Vicente, J. Martin, M.T. Chicote, X. Solans and C. Miravitlles, J. Chem. Soc., Chem. Commun., (1985) 1004.

2 J. Vicente, A. Arcas, M.V. Borrachero and M.B. Hursthouse, J. Chem. Soc. Dalton Trans., (1987) 1655; J. Vicente, M.T. Chicote, J. Martin, M. Artigao, X. Solans, M. Font-Altaba and M. Aguilo, ibid., (1988) 141.

3 (a) J. Vicente, M.T. Chicote, J. Martin, P.G. Jones, C. Fittschen and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1986) 2215; J. Vicente, M.T. Chicote, J. Martin, P.G. Jones and C. Fittschen, ibid., (1987) 881; (b) J. Vicente, J.A. Abad, F. Teruel, and J. Garcia, J. Organomet. Chem., in the press.

4 J. Vicente and M.T. Chicote, Inorg. Chim. Acta, 54 (1981) L259; J. Vicente, M.T. Chicote, and M.D. Bermudez, ibid., 63 (1982) 35; J. Vicente, M.T. Chicote, A. Arcas, and M. Artigao, ibid., 65 (1982) L251; J. Vicente, M.T. Chicote, A. Arcas, M. Artigao and R. Jimenez, J. Organomet. Chem., 247 (1983) 123; J. Vicente, M.T. Chicote, M.D. Bermudez, ibid., 268 (1984) 191; J. Vicente, M.T. Chicote, M.D. Bermudez, M.J. Sanchez-Santano, P.G. Jones, C. Fittschen, and G.M. Sheldrick, ibid., 310 (1986) 401; J. Vicente, A. Arcas, and M.T. Chicote, ibid., 252 (1983) 257; J. Vicente, M.T. Chicote, M.D. Bermudez, X. Solans, and M. Font-Altaba, J. Chem. Soc. Dalton Trans., (1984) 557.

5 J.L. Brianso, X. Solans, J. Vicente, J. Chem. Soc., Dalton Trans., (1983) 169.

6 P. Fitton, J.E. McKeon, and B.C. Ream, J. Chem. Soc., Chem. Commun., (1969) 370; P.S. Fitton and E.A. Rick, U.S. Pat. 3674825. Chem. Abstr., 77 (1972) 88664.

7 S.H. Mastin, Inorg. Chem., 13 (1974) 1003.

8 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley and Sons, Inc., 4th., 1986, p. 254.

9 D.R. Coulson, Inorg. Synth., XIII (1972) 121.